



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P02053	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NO 02/00400	International filing date (day/month/year) 01.11.2002	Priority date (day/month/year) 01.11.2002
International Patent Classification (IPC) or both national classification and IPC C01B21/48		
Applicant NORSK HYDRO ASA et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 5 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the opinion</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input type="checkbox"/> Certain observations on the international application</p>		
Date of submission of the demand 30.09.2003	Date of completion of this report 02.11.2004	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Grundke, H Telephone No. +49 89 2399-8564 	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NO 02/00400

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1, 2 as published
3-7 received on 15.10.2004 with letter of 12.10.2004

Claims, Numbers

1-11 as published

Drawings, Sheets

1/1 as published

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

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5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-11
	No: Claims	
Inventive step (IS)	Yes: Claims	1-11
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-11
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NO 02/00400

Item V:

Reference is made to the following document:

D1: GB 510 053 A

D1 describes a method for crystallisation of alkaline earth metal nitrates. D1 addresses the problem related to the solidification of melts containing calcium nitrate and magnesium nitrate, which salts tend to remain in a liquid viscous condition instead of solidifying. In order to overcome this problem an ammonium salt is admixed.

The present claimed invention is able to produce ammonium free calcium nitrate that easily solidifies. Industrial production of solid non-crystalline nitrates without ammonium has been impossible prior to the claimed invention.

Thus the invention surprisingly enables the production of all kind of nitrates or mixtures of nitrates that are difficult to solidify.

Therefore present claims 1-11 meet the requirements of N, IS and IA.

JC14 Rec'd PCT/PTO 29 APR 2005

phases is added to the melt. Melt drops are then formed and allowed to cool and solidify during up to 70 seconds, preferably 20-70 seconds. It is preferred to use a cooling belt for solidification of the particles. The belt is cooled by air, water, oil or another medium.

- 5 The melt temperature is preferably kept 0-10 °C below the crystallization point of the melt. When calcium nitrate particles are produced, $\text{CN} \cdot 2\text{H}_2\text{O}$ and $\text{CN} \cdot 3\text{H}_2\text{O}$ are used as seed particles. The particles formed have a particle size between 0,2 and 0,8 mm, preferably between 0,4 and 0,6 mm. Particles could be made from a melt consisting of 74 weight % calcium nitrate, 14 weight % potassium nitrate and 12 weight % water. Solid
- 10 particles can also be produced consisting of a homogenous mixture of nitrates, chlorides and crystal water. An example of this is particles made from a melt consisting essentially of 50 weight % calcium nitrate, 4 weight % ammonium nitrate, 26.5 weight % calcium chloride and 18-20 weight % water.
- 15 Several experiments were carried out in order to try to make particles of the melts.

Example 1 – Granules (For comparison)

CN-water solutions were evaporated to above 70, 75 and 78 weight % CN .

- The various melts were sprayed onto a rotating laboratory pan granulator containing
- 20 solid NH-CN (calcium nitrate from Norsk Hydro ASA) in various ratios and at various temperatures.

- None of the trials succeeded as the liquid/melt did not solidify . The whole matrix (solid CN+melt) turned into a sticky slurry that could not be processed with liquid/solid ratios
- 25 within acceptable limits.

Example 2 – Prills (For comparison)

- Melts with the CN concentrations mentioned above, were kept at temperatures close to the
- 30 crystallization point given by the literature. Finely crushed NH-CN were mixed into the melt subsequent to pumping the melt at high pressure to nozzles where drops were formed and allowed to cool down to 20 °C for 5-10 seconds.

As cooling medium oil and air were tried. Solid particles did not form due to under-cooling.

5 Example 3 - Making pastilles

Trial 1 (For comparison):

Droplets of CN-melts with CN concentrations above 70, 75 and 78 weight % pure CN where allowed to cool on a chilled metal plate down to 10°C for several minutes.

- 10 The melt-drops turned into viscous, sticky liquid, solid particles did not form.

Trial 2 (For comparison):

- 15 Same procedure as above but now finely divided solid CN powder was added to the melt before setting the droplets on the plate. Solids of NH-CN and crushed $\text{CN} \cdot 4\text{H}_2\text{O}$ crystals were applied .

The melt-droplets turned into slurries with no particle strength as they cooled down.

- 20 Trial 3 (according to the invention):

CN melt having 23 weight % water and 77 weight % CN were allowed to cool on a plate for 48 hours at 20°C. A white solid material was formed during this time

- 25 Now clearly the melt had turned into a strong solid material over these hours and X-ray analysis showed that the material consisted of $\text{CN} \cdot 2\text{H}_2\text{O}$ and $\text{CN} \cdot 3\text{H}_2\text{O}$.

However, the solidifying time was too long for a convenient particulation process.

Trial 4a (according to the invention):

- 30 Same procedure as in trial 1, but now a CN-melt consisting of 23 weight % water and 77 weight % CN was cooled down to 50-55°C and 2 weight % crushed material from trial 3 was thoroughly mixed into the melt.

As the drops cooled, crystals were formed and during 30-70 second hard pastilles were formed with particle strength above 1 kg. As time passed, particle strength became substantially higher.

- 5 Particles did form with this procedure and the crucial part of this procedure was obviously to add finely divided solid material consisting of the equilibrium phases of the system at room temperature. (CN*2H₂O and CN *3H₂O)

Trial 4b (according to the invention):

- 10 Same procedure as trial 4a but now melt composition was 25 weight %/ 75 weight % and 21.5 weight %/ 78,5 weight % (H₂O/CaN).

Trial 5 (according to the invention):

- 15 Same procedure as in Trial 4, after reducing the temperature of the melt (23% weight % H₂O/77% weight % CN) to approximately 45°C the finely divided solid material was mixed in as seeding particles. As crystals started to form in the beaker, drops were allowed to fall on the cooling plate and simultaneously pure melt (23 weight %/ 77 weight %) with temperature below 50°C was added to the beaker, while stirring.

20

In this way drops containing solid crystals with the right composition were continuously formed and solidified on the metal plate just by adding one portion of solid material to make the crystallization start.

- 25 However, 40-70 seconds are too long time for using a granulation or prilling technique with an acceptable recycling ratio.

To use procedure 5 for producing large quantities of particles, a way of obtaining 40-70 second crystallization time was looked for.

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Example 4 – Making CN pastilles in industrial scale (according to the invention)

Experiments were carried out on a moving steel cooling belt (as described in US patent
5 No. 5326541) that is kept at a low temperature by using water as cooling agent. On this
belt a rotating drum with nozzles, supply drops that can solidify on the belt. A plant test
was carried out with CN melt (23 weight %/ 77 weight %).

By using procedure described in "Trial 5", several hundred kg of CN particles (pastilles)
10 were produced on the cooling belt.

Example 5 – Making MgN pastilles (according to the invention)

Trial 5 in Example 3 was repeated by replacing CN melt with 1: MgN-water melt having
15 composition 67 weight % MgN and 33 weight % H₂O (boiling point 180 °C) and 2: MgN-
water melt with composition 58 weight % MgN and 42 weight % (boiling point 155°C).
Both melt 1 and 2 were cooled down to 30 °C by procedure mentioned in trial 5 (Example
3). Letting composition 1 and 2 solidify in an exsiccator for 3 days, and then crush the
solids formed into a fine powder made seeding material.

20 With melt 1 and 2 and the procedure described we obtained MgN*4H₂O and MgN *6H₂O
respectively. MgN*6H₂O was made also without seeding material as the MgN*6H₂O melt
very easily solidified.

25 Example 6- Making pastilles of MgN-AN and CN (according to the invention)

A melt consisting of 67 weight % CN, 4.0 weight % AN, 10 weight % MgN and 20
weight % water was held at 110°C. The melt was cooled down to 65°C and seeding
material thoroughly mixed in as drops were allowed to fall on a cold metal plate.

30

During 60 seconds on the plate hard pastilles were formed . Letting the melt composition
crystallize in an exsiccator for 2-3 days and then grinding to a fine powder made seeding
material.

Example 7- Mixture of CN, AN and CaCl₂ (according to the invention)

A melt consisting of 50 weight % CN, 4 weight % AN, 26.5 weight % CaCl₂ and 18-20 weight % water was made by melting a mixture of NH-CN and CaCl₂*2H₂O (130-140°C).

- 5 By using procedure described in 4 b (seeding material added at 120 °C) nice particles were formed within 30 seconds on a cold steel plate. The particles consisted of homogenously solidified CaN-AN CaCl₂ particles.

10 Example 8 – Mixture of CN and KN (according to the invention)

A melt consisting of 74 weight % CN, 14 weight % KN and 12 weight % water was made by evaporating water from a CN -KN -H₂O solution. The melt temperature was reduced to 86°C, app. 5-6 °C above crystallization point. 3 weight % finely grained seed material was thoroughly mixed in and droplets allowed falling on to a cold metal plate
15 (23°C).

During 50-60 seconds hard pastilles/particles formed on the plate.

- 20 The right seeding material was made by letting the melt composition crystallise in an exsiccator over 2-3 days and then grind to powder the solid formed.

Thus, by applying:

- 25 -correct melt or CN-water composition
-correct temperature of the melt (at or below cryst. point)
-correct seeding material (consists of equilibrium phases of the solidifying material)
- a cooling belt or a similar system that allows 20-70 seconds or more for crystallization ,

- 30 it has been possible to find a procedure for producing solid CN particles (CN+crystal water) without AN. The procedure can be applied for making solids of several nitrate systems containing Ca, Mg, K, Na, NH₄ or mixtures of these nitrates or mixtures of nitrates and chlorides.